

Distribution of the stable isotopes ($\delta^{18}\text{O}$, δD и $\delta^{13}\text{C}$) in natural waters of the Baydar valley (Crimean Peninsula)

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Abstract. Results of the study of the stable isotopes ($\delta^{18}\text{O}$, δD and $\delta^{13}\text{C}$) distribution in natural waters of the Baydar valley (southwestern part of the Crimean Peninsula) are presented. The study region holds fresh and ultra-fresh waters of predominantly bicarbonate calcium composition with TDS varying from 194 to 1137 mg/dm³. The research results revealed that all of the studied waters are of atmospheric origin that lie either along the global (GMWL) or local (LMWL) meteoric water lines. The established variations are: from -9.5 to -5.6‰ for $\delta^{18}\text{O}$ values in waters with δD values varying from -64.0 to -40.0‰. The source for bicarbonate ion enriched in $\delta^{13}\text{C}$ in natural waters of the Baydar valley are carbonate sedimentary rocks, atmospheric carbon dioxide and organic compounds. Surface waters have heavier isotopic composition $\delta^{13}\text{C}$ (-9.2 – -7.0‰) because of the atmospheric CO₂. Artesian waters are differentiated by lighter $\delta^{13}\text{C}$ (-12.8 – -10.7‰) due to the interactions between carbonate rocks and the dispersed organic matter. Water sources (springs, wells) are characterized by the widest variations of $\delta^{13}\text{C}$ (-6.9 – -15.5‰) due to the presence of the atmospheric CO₂ and intense processes of biochemical decomposition of organic compounds in the soil layer.

1 Introduction

Oxygen, hydrogen and carbon isotope ratios prove to be the only signature of the chemical composition of natural waters, allowing to study their evolution by direct methods, which is why the use of stable isotopes ($\delta^{18}\text{O}$, δD and $\delta^{13}\text{C}$) have become widely

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popular in different studies of natural waters, whether they are concerned with their dynamics, origin, or hydrogeochemical effects in the water-rocks interactions [1]. Until recently, there existed no systematic data on the isotopic composition of atmospheric precipitation on the Crimean Peninsula, which was aggravated by very few hydrogeochemical investigations and isotope studies on natural waters [2]. Among the latest research into these problems, we should mention the works by Y. V. Dublyansky, A. B. Klimchouk, G. N. Amelichev, S. V. Tokarev, K. Shpyotl, E. P. Kayukova [2-3]. The object of this research is natural waters of the picturesque Baydar valley located in the southwestern Crimean Peninsula within the Balaklava district of the Sevastopol city agglomeration. From the southern and eastern sides, the valley is immediately adjacent to the main ridge of Crimean mountains (Foros, At-Bash, Ay-Petri and others). The main groundwater resources of the study area are associated with the Upper Jurassic aquifer complex, playing a key role due to its connection with the main headwater systems and their recharge source within the three hydrogeological structures: the inland Crimean Plain, the Azov-Kuban artesian basins and hydrogeological folded region of mega-anticlinorium of the Mountainous Crimea. This complex is best studied within the Rodnikovskoe water intake in the Baydar valley. From the hydrogeochemical point of view, natural waters of the region are largely underexplored [2, 4-6]. This paper discusses results of the latest field research (October 2018) dedicated to comprehensive isotope-hydrogeochemical studies of natural waters of 25 natural water outlets.

2 Results and discussion

The chemical analyses of natural waters were carried out at the Vinogradov Institute of Inorganic Chemistry SB RAS (Novosibirsk), the isotopic compositions ($\delta^{18}\text{O}$, δD and $\delta^{13}\text{C}$) were studied at the Sobolev Institute of Geology and Mineralogy RAS (Novosibirsk). When combined, their results revealed that fresh and ultra-fresh waters of mainly bicarbonate calcium composition with TDS from 194 to 1137 mg/dm³ are widespread in the region (Fig. 1a). The studied natural (surface, ground and artesian) waters differ significantly in their chemical composition: *artesian waters* with TDS 254-832 mg/dm³ and neutral pH value (6.98-7.54); higher mineralized *groundwaters* (up to 1137 mg/dm³) with widely varying pH values (from 7.18 to 8.31); and *surface waters* (the Chyornaya river and Chernorechensk water reservoir) with TDS between 194 and 288 mg/dm³ and slightly alkaline pH (8.02-8.04). The interpretation of stable-isotope analyses data is commonly based on the Craig's line, also known as Global Meteoric Water Line (GMWL) [7]: $\delta\text{D} = 8.0 \cdot \delta^{18}\text{O} + 10$. Given a certain combinations of climatic and geographical parameters, the inter-relations of stable isotopes, while remaining linear, may differ from the above equation. As such, the relationships are defined according to the Local Meteoric Water Line (LMWL), which is expressed as: $\delta\text{D} = 7.0 \cdot \delta^{18}\text{O} + 3.2$ for the northern slope of the Crimean Mountains (as proposed by Y.V. Dublyansky and co-authors) [2]. In fact, the accumulation of experimental data on the isotopic composition of groundwater of the Crimean Peninsula has just begun. Fig 1b shows the results of $\delta^{18}\text{O}$ and δD isotope analysis for natural waters of 25 water outlets of the Baydar valley, as follows: 6 wells of Rodnikovskoe groundwater deposit; springs: Skel'sky (basic), Kolkhozny-southern, Kolkhozny-northern, Kara-Agach, Stranny, Varnaly fountain, Fuska-Chokrak, Laspi observation deck, Despit, in the vicinity of the Church of the Resurrection of Christ, Sanatory-upper, Sanatory-lower, Kilse-Burun, Kuyu-Alan, Chertova Lestnitsa, Q-044, Merdven-Kayasy; surface waters: Chyornaya river and Chernorechensk reservoir.

The figure explicitly demonstrates that the $\delta^{18}\text{O}$ and δD isotope ratios for all the water exposures are in good agreement with the Local Meteoric Water Line. The three groups of natural waters are described below. The first group is represented by surface waters (the

Chyornaya river, Chernorechensk water reservoir and Fuska-Chokrak and Kilse-Burun springs) and characterized by the stable-isotope ratios: $\delta^{18}\text{O} = -7.5 - -5.6 \text{ ‰}$ and $\delta\text{D} = -52.0 - -40.0 \text{ ‰}$. The second group ($\delta^{18}\text{O} = -9.7 - -8.9 \text{ ‰}$ and $\delta\text{D} = -64.0 - -54.0 \text{ ‰}$) includes groundwaters of the Rodnikovskoe water intake employing Upper Jurassic headwater water-bearing complex as the recharge supply and showing a hydraulic affinity with Skel'sky spring (basic source); and waters from cave springs Skel'sky, Chyornaya and Mamut-Chokrak. At this, the data obtained by Y.V. Dublyansky and co-authors [2] suggest that waters from the aquifer within the Upper Jurassic limestone unit (tested in the observation well in the northeastern part of the Baydar valley) submerged below the erosional incision level of the Krasnopeshernaya river have the following isotope ratios: $\delta^{18}\text{O} = -12.9 \pm 0.2 \text{ ‰}$ and $\delta\text{D} = -83.0 \pm 1.0 \text{ ‰}$. The third group occupies an interim position between these two brackets most of the studied water springs and wells. The established isotope ratios are $\delta^{18}\text{O} = -9.3 - -7.9 \text{ ‰}$ and $\delta\text{D} = -61.0 - -51.0 \text{ ‰}$.

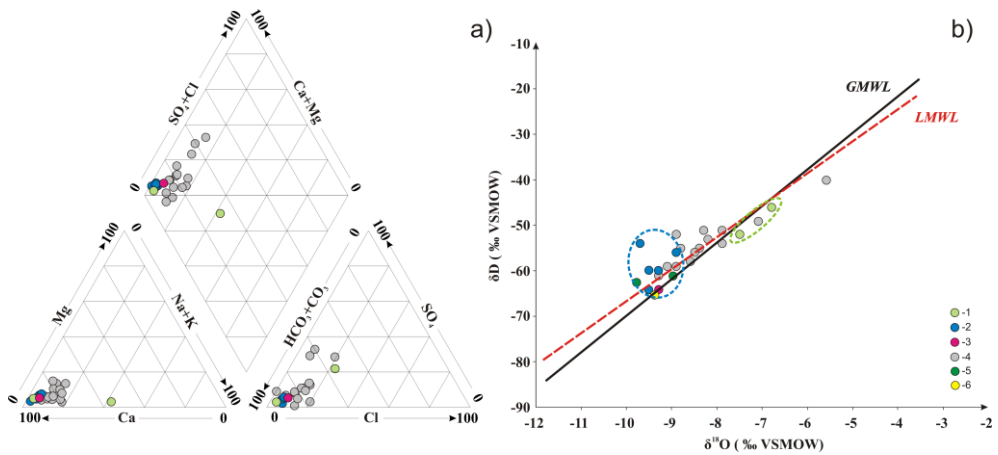


Fig. 1. Piper diagram (a) and $\delta^{18}\text{O}$ and δD isotopic composition in natural waters of the Baydar valley (b): 1 – surface, 2 – artesian, 3 – Skel'sky spring, 4 – water sources (springs and wells), cave-water sources [2]; 5 – Skel'skaya and Chyornaya, 6 – Mamut-Chokrak. GMWL [7], LMWL [2].

The hydrologic cycle maintains constancy of the isotopic composition of meteoric and surface waters, depending on the latitude, altitude and mean annual surface temperature (MAST) in the area. The heavy isotopes ^{18}O and D concentrations in the atmospheric precipitations depend on the condensation (dewpoint) temperature and varies widely (heavy isotopes are fewer in snow than in rain) [1]. In this regard, the second group of natural waters is assumed to be dominated by the winter water balance due to recharge from snow melting. In addition to $\delta^{18}\text{O}$ and δD , we studied the $\delta^{13}\text{C}$ isotope ratios distribution in natural waters of the Baydar valley (Fig. 2a). Carbonate sedimentary rocks, atmospheric carbon dioxide and organic compounds have proven to be the source of bicarbonate ion in natural waters of the Baydar valley. Surface waters complexed with the atmospheric CO_2 have heavier $\delta^{13}\text{C}$ values ($-9.2 - -7.0 \text{ ‰}$). They also show an affinity with the isotopic composition of secondary calcites ($\delta^{18}\text{O} = -9.4 - -7.6 \text{ ‰}$ and $\delta^{13}\text{C} = -9.9 - -7.7 \text{ ‰}$), indicating the involvement of the former in the processes of their formation. Artesian waters are characterized by lighter $\delta^{13}\text{C}$ values ($-12.8 - -10.7 \text{ ‰}$), inasmuch as there is a trade-off between the carbon isotopes of HCO_3^- ion (dominant in the anionic composition) and dispersed organic matter which entered into the water in the form of CO_2 during the diagenesis. According to research findings by Y.V. Dublyansky and co-authors, variation of the stable-isotope ratios within the unaltered limestones are fairly low and constitute: $\delta^{18}\text{O} = -4.1 - -1.2 \text{ ‰}$ and $\delta^{13}\text{C} = +0.7 - +1.8 \text{ ‰}$ [8]. Water sources (springs, wells) are characterized by the widest variation of $\delta^{13}\text{C}$ ($-6.9 - -15.5 \text{ ‰}$) due to the presence of

atmospheric CO₂, on the one hand, and the active biochemical processes of organic compounds decomposition in the soil layer, on the other hand. The trends established for the carbon stable isotope δ¹³C behavior are described as: increasing as alkalinity of natural waters increases (Fig. 2b) and decreasing with an increase in TDS values (Fig. 2c, d).

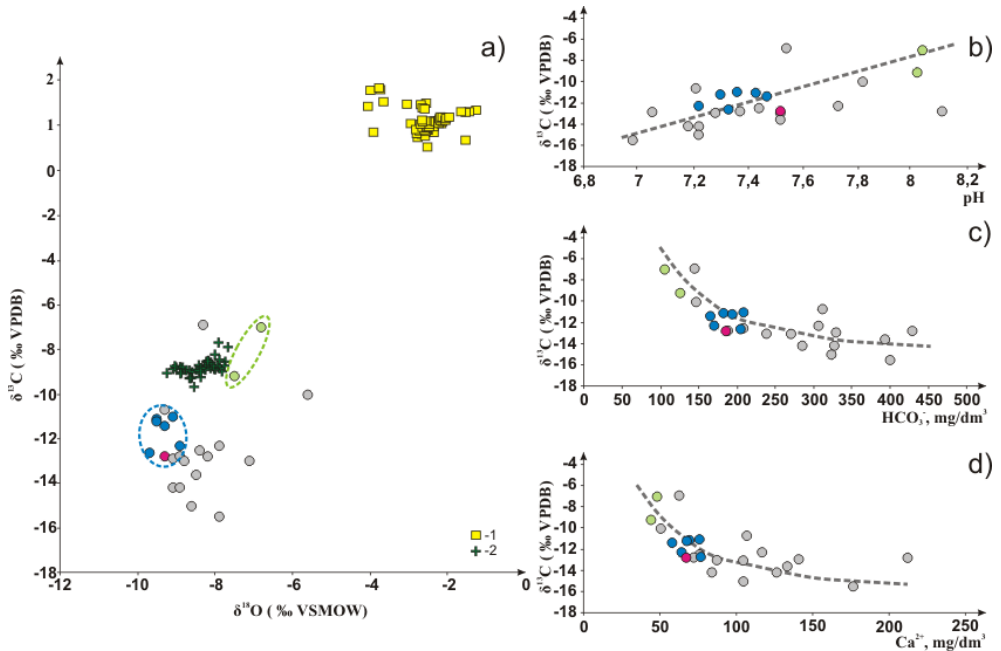


Fig. 2. The isotopic composition δ¹⁸O and δ¹³C (a) and the dependence of δ¹³C on pH (b) and the amounts of bicarbonate ion (c) and calcium (d) in natural waters of the Baydar valley. The δ¹⁸O and δ¹³C isotopic composition [8]: 1 – unaltered Paleocene and Eocene limestones in the southwestern part of the Inland ridge of the Crimean Mountains, 2 – the secondary calcite from Besh-Kosh cave.

3 Conclusions

All of the studied natural waters of the Baydar valley are of atmospheric origin and lie along the global (GMWL) and local (LMWL) line of meteoric waters. The three identified groups of water inferred from the isotope-hydrogeochemical data are described below.

The first group of waters is ranked as isotopically "heavier" because of the active exchange between the water and the atmosphere, combined with active processes of evaporation and degassing of water, which, according to [9] can significantly "weigh down" the carbon isotope ratio. This group is represented by surface waters (the Chyornaya river, Chernorechensk water reservoir and Fuska-Chokrak and Kilse-Burun springs) and is characterized by the following isotope ratios: δ¹⁸O = -7.5 – -5.6 ‰, δD = -52.0 – -40.0 ‰ and δ¹³C -9.2 – -7.0 ‰. The second group represents stable carbon isotopes ratios δ¹³C, "lighter" due to a lower exchange between carbon isotopes of artesian waters and the atmosphere (virtually without involvement of the water evaporation and degassing processes), and the presence of the organic matter decomposition with the affiliated liberation of isotopically "light" CO₂. This group embraces groundwaters from the Rodnikovskoe water intake, Skel'sky source (basic) and waters sourced from cave springs (Skel'sky, Chyornaya and Mamut-Chokrak) which have isotope ratios written as: δ¹⁸O = -9.7 – -8.9 ‰, δD = -64.0 – -54.0 ‰ and δ¹³C -12.8 – -10.7 ‰. The third group is for water sources, where all the above discussed processes are included: from the isotopic exchange

between water and the atmosphere and active participation of water evaporation and degassing to their saturation with "light" isotopes released during the active processes of biochemical transformation of organic compounds in soil. Both the prevalence and, contrariwise, localization of certain processes lead to such large variations in $\delta^{13}\text{C}$ ratios, their relations established by this research are given below: $\delta^{18}\text{O} = -9.3 - -7.9 \text{ ‰}$, $\delta\text{D} = -61.0 - -51.0 \text{ ‰}$ and $\delta^{13}\text{C} = -6.9 - -15.5 \text{ ‰}$.

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References

1. V.I. Ferronsky, V.A. Polyakov, *Hydrosphere isotopy*, Moscow: Nauchnyi mir, 632 (2009)
2. Yu.V. Dublyansky, A.B. Klimchuk, G.N. Amelichev, S.V. Tokarev, K. Shpetl, *The isotopic composition of atmospheric precipitation and karst sources on the northwestern slope of the Crimean Mountains*, *Speleology and karstology*, **9**, 14-21 (2012)
3. E.P. Kayukova, *Formation of the isotopic composition of natural waters of the Mountain Crimea under the influence of natural processes*, *Vestnik of Saint Petersburg University Series 7. Geology. Geography*, **2**, 11-26 (2016)
4. V.M. Artemenko, Yu.P. Ilyin, V.S. Kucherenko, A.I. Ryabinin, S.A. Bobrova, A.N. Gutsalyuk, Yu.A. Malchenko, L.V. Saltykova, *Hydrochemical regime and trace element composition of the waters of the Chernorechensky reservoir in 1991-2004*, *Ekologicheskaya bezopasnost pribrezhnoy i shelfovoy zon i kompleksnoye ispolzovaniye resursov shelfa*, **12**, 129-149 (2005)
5. G.N. Amelichev, *Skelskaya Cave: State of art of the study, problems of protection and use*, *Speleology and Karstology*, **1**, 94-99 (2008)
6. R.Y. Minkovskaya, A.V. Ingerov, *Hydrochemical characteristics of the rivers of the Sevastopol region*, *Ekologicheskaya bezopasnost pribrezhnoy i shelfovoy zon i kompleksnoye ispolzovaniye resursov shelfa*, **22**, 265-281 (2010)
7. H. Craig, *Isotopic variations in meteoric waters*, *Science*, **133** (3465), 1702-1703 (1961)
8. Yu.V. Dublyansky, A.B. Klimchuk, A. B. Timokhina, G.N. Amelichev, K. Shpetl, *Changes in the isotopic composition of rocks in the near-wall zones of hypogenic karst canals of Piedmont Crimea*, *Speleology and karstology*, **10**, 58-75 (2013)
9. P.J. Mickler, P. Carlson, J.L. Banner, D.O. Breecker, L. Stern, A. Guilfoyle, *Quantifying carbon isotope disequilibrium during in-cave evolution of drip water along discreet flow paths*, *Geochimica et Cosmochimica Acta*, **244** (1), 182-196 (2019)